MOLECULAR MODELING STUDIES OF BITUMINOUS COAL STRUCTURE[*]

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Keywords: molecular modeling; computer-aided molecular design; coal structure

Abstract

Computer-aided molecular design (CAMD) has been used to define the structural conformations and intramolecular interactions of bituminous coal models. Molecular dynamics studies have produced representative minimum energy conformations for several published molecular models. These studies show the importance of van der Waals (vdW) and hydrogen-bonding interactions as cohesive forces responsible for the three-dimensional (folded) structures of the coal models. Calculations on pairs of small ring compounds representative of those found in coal clusters demonstrate that aromatics exhibit stronger vdW interactions compared with saturated ring compounds. Correlations of the vdW interactions with boiling points also show differences between aromatics and saturated rings.

Introduction

Details of coal structure and the nature of bonding within the coal structure are key concepts as one attempts to develop an understanding of coal reactivity. Because of the strong connection between structure and reactivity, there have been many studies directed toward a definition of coal structure. One group of studies has been concerned with the molecular structure of coal, as defined by various chemical and physical properties. Examples of molecular models postulated for bituminous coal are given in references 1-4. Because coal is a highly heterogeneous material, these models are only intended to be representative, or average, structures. These structures generally consist of 2-4 ring polyaromatic hydrocarbons (clusters) containing appropriate numbers of heteroatomic constituents. Most of these clusters are connected together by hydroaromatic, etheric or aliphatic linkages; others remain unconnected and relatively mobile.

The second major emphasis of bituminous coal structure studies has been to define coal as a network solid, i.e., as clusters connected together by three-dimensional cross-links (5-10). In these network models, the average size of clusters and the number of clusters between cross-links are relevant factors, while the molecular details of the clusters are relatively unimportant. Studies assuming a cross-linked structure support the concept that hydrogen bonds within the coal structure are largely responsible for defining the secondary structure of bituminous coal (6,7,9,10). The network models also explain qualitatively the observed solvent-swelling behavior of bituminous coal (6). Bituminous coals swell when intramolecular hydrogen (and perhaps other non-covalent) bonds are broken and replaced with coal-solvent hydrogen bonds. The most effective swelling solvents are those that form strong hydrogen bonds, and thus replace most or all of the original intramolecular hydrogen bonds. However, even with strong solvents, the degree of swelling is ultimately limited by the covalent cross-link structure of the coal, which is unaffected by the solvent. Thus, the extent of solvent swelling is related to the covalent cross-link density.

In this paper, we explore the relative importance of hydrogen bonding and van der Waals (vdW) interactions in energy-minimized coal molecular structures. While hydrogen bonding has been more widely recognized as a major contributor to the stability of middle-rank coals, vdW interactions have also been characterized as important (7,11), especially for higher-rank coals (> 87% C, daf), which contain larger, predominantly aromatic, ring systems (12). Additional support for the importance of vdW interactions in middle-rank coals is found in the work of White (13), who concluded that vdW forces were most likely the dominant intermolecular forces in liquids derived from Illinois No. 6 coal. To the extent that these liquids are similar in structure to the clusters in the coal from which they are derived, vdW interactions would be expected to be of importance for the coal as well. It has generally been found that coal-derived liquids have molecular structures similar to the parent coal (3), providing support for this view.

Method

As previously described (14), the CAMD studies were carried out using a commercial molecular modeling software program (BIOGRAF, BioDesign, Pasadena, CA), operating on a MicroVAX II computer coupled with an Evans and Sutherland PS390 graphics terminal. The CAMD software allows the construction of molecular structures of desired complexity (up to several thousand atoms) and the subsequent manipulation of those structures using molecular dynamics techniques to determine most probable (i.e., minimum-energy) structures.

The molecular dynamics calculations employ a force field model (15) that describes the potential energy of a structure in terms of interactions between covalently-bonded atoms (bond stretches, angle bends, torsions, inversions) and other, generally longer-range, interactions between non-bonded atoms (van der Waals, electrostatic and hydrogen-bond interactions). BIOGRAF uses DREIDING (16), a force field that treats a wide range of atoms and atom types.

In this paper, we focus primarily on the vdW and hydrogen bond interaction energies calculated for structures before and after molecular dynamics (energy minimization) runs. VdW interaction energies (E_{vdW}) are calculated in DREIDING using a Lennard-Jones 12-6 potential, with vdW bond strength (well depth) D_0 and equilibrium bond length R_0 defined separately for each type of atom pair.

$$E_{vdW}(R) = D_0 \bullet \left\{ \left[\frac{R_0}{R} \right]^{12} - 2 \left[\frac{R_0}{R} \right]^6 \right\} \bullet S \qquad 1)$$

A switching function S is employed to gradually "cut off" the vdW calculations for atom pairs more than 8 angstroms apart. Separate calculations showed that using this cutoff affected the calculated vdW energies by 3% or less, while reducing the time required for the calculations by 4-7 times for the structures being studied (for example, for the modified Shinn structure, containing 1040 atoms, over 500,000 vdW interactions must be calculated in the absence of a distance cutoff. With a cutoff between 8 and 9 angstroms, the number of vdW interactions calculated is reduced to ~75,000).

Hydrogen bond interaction energies (E_{hb}) are calculated using a Lennard-Jones 12-10 potential with an additional dependence on the angle between acceptor atom (A), hydrogen atom (H), and donor atom (D).

$$E_{hb}(R) = D_0 \bullet \left\{ 5 \left[\frac{R_0}{R} \right]^{12} - 6 \left[\frac{R_0}{R} \right]^{10} \right\} \bullet \cos^2(\theta_{AHD}) \bullet S \qquad 2)$$

All oxygen, nitrogen and sulfur atoms are considered to be potential hydrogen bond acceptors and donors. For all atom types, the equilibrium distance R_0 between donor and acceptor is defined to be 2.75 angstroms, and the equilibrium hydrogen bond strength D_0 is fixed at 9.50 kcal/mol. Since DREIDING uses the same force constants for all hydrogen bonds independent of atom types, energy calculations can be compared for one structure relative to another (providing the relative numbers of heteroatoms are similar, as in the present case), but are not accurate in absolute terms.

Calculations of hydrogen bonding and vdW interaction energies were carried out for three molecular models of bituminous coal, those of Wiser (2), Solomon (3), and Shinn (4), modified as previously described (17). Stabilization energies were determined as the differences in vdW and hydrogen bonding energies for the energy-minimized structures (after molecular dynamics calculations) relative to the initial structures. VdW interactions were also calculated for pairs of simple ring compounds ranging in size from C_6 (benzene and cyclohexane) to C_{24} (coronene and perhydrocoronene). The range of sizes and the extremes of fully-aromatic to fully-hydrogenated molecules were intended to cover the range of molecular cluster sizes and compositions believed to be present in bituminous coal. In each case, two molecules (e.g., two benzenes) were first separated by a sufficient distance to eliminate any intermolecular vdW interactions (~ 20 angstroms), and the total (intramolecular) vdW energy of the two molecules calculated. The molecules were then allowed to attain a minimum-energy configuration and the vdW energy again calculated. The difference in the two energies was taken to represent the vdW stabilization energy per molecular pair.

Results

Table I shows data related to hydrogen bond formation for each of the models studied. The total number of potential hydrogen bond donors and acceptors for each structure is given, as well as the actual number of intercluster hydrogen bonds formed in the energy-minimized molecular structures. Some additional intracluster hydrogen bonds were observed (i.e., hydrogen bonds between acceptors and donors present on the same cluster, on either the same or adjacent rings), but these do not contribute stability to the folded structure. Interestingly, although the Wiser model had the highest number of donors and acceptors relative to the total number of atoms, it exhibited the least intercluster hydrogen bonding. This was apparently because the donors and acceptors in the Wiser model are most often in close proximity, and preferentially form intracluster hydrogen bonds. The observation may also be partly due to the generally higher degree of cross-linking between clusters observed for the Wiser structure. This strong cross-linking appears to have limited the freedom of the clusters to move relative to one another, and thus may have restricted the access of intercluster donors and acceptors to each other. The average energy calculated for the intercluster hydrogen bonds for all models ranged from 4.5 to 7.9 kcal/mol, in good agreement with Larsen's data based on solvent swelling interactions (5-8.5 kçal/mol, ref. 6). The calculated values are somewhat lower than the maximum calculated bond strength (9.5 kcal/mol, Eq. 2), reflecting less than optimal hydrogen bond angles and bond lengths.

The number of vdW interactions in the energy-minimized structures and the vdW stabilization energies are also given for each model. The stabilization energy was calculated as the difference between the vdW energy of the initial structure and of the energy-minimized structure. As shown, although the number of vdW interactions for each structure is quite large (even with the assumed vdW cutoff distance), the energy per interaction is very small (~ 0.005 kcal).

Finally, the differences between the vdW and hydrogen bond energies for each model before and after energy minimization were compared, to evaluate their relative contributions to stabilization of the secondary structure. As Table I shows, the vdW stabilization energy was in every case greater than that due to hydrogen bond formation by roughly a factor of 2-3. It is not obvious how to compare the relative importance of vdW and hydrogen bonding interactions based on these total energy data, which sum up tens of thousands of vdW

interactions but only tens of hydrogen bonding interactions. However, it does seem clear from these data that vdW interactions are significant contributors to bituminous coal structural stability.

To further evaluate the significance of vdW interactions in coal, vdW interactions were calculated for pairs of simple aromatic and saturated-ring ring compounds ranging in size from C_6 (benzene and cyclohexane) to C_{24} (coronene and perhydrocoronene). Figure 1 shows the vdW stabilization energies for each molecular pair, normalized to the number of carbon atoms in each molecule and plotted against the molecular weight of the molecule. For the aromatic molecules, there is a well-defined progression toward greater stabilization energy (per carbon atom) with ring size. This is to be expected, since there are more vdW interactions possible for larger molecules. By contrast, for the fully-saturated rings, the vdW stabilization per carbon tends to be smaller than for the aromatics and is relatively unchanged with ring size. Apparently the steric overlap of the non-planar hydrogens in the saturated ring compounds prevents the molecular pairs from approaching to optimal distances for C-C vdW interactions (the C-C distance for equivalent carbons in the aromatic ring pairs is ~ 3.5-3.7 angstroms, relatively near to the equilibrium vdW C-C distance of 3.9 Angstroms; for the saturated ring pairs, the C-C distance ranges from 4.7-5.1 angstroms).

These calculations may overestimate somewhat the vdW interactions for the aromatic ring compounds. The calculated minimum-energy conformations for all the molecular pairs are with rings in a face-to-face parallel configuration. However, Larsen has reported that quadrupole interactions for aromatic ring compounds (which are not calculated in most force field approximations) are repulsive for a parallel ring configuration, and tend to to force rings to orient in a perpendicular (T-shaped) fashion (18). The tendency to form non-planar pairs is strongest for small rings (e.g., benzene), and weakest for large rings. If quadrupole effects were included, vdW interactions for benzene might be reduced by roughly 50%, but for coronene by less than 20% (19). Thus, the actual progression of vdW stabilization energy with size for aromatic ring compounds would likely be 'even more pronounced than Fig. 1 indicates. The effects of quadrupole interactions on the orientation of saturated ring pairs are not known.

Figure 1 also shows the vdW stabilization energies for the three coal structures previously discussed, expressed in terms of the average molecular cluster size. The average molecular cluster size for each structure was obtained after dividing the structure into "clusters" at apparent linkage sites (aliphatic, etheric bridges, etc.). These coal structure stabilization energies represent all the interactions of the molecular clusters, not just those of pairwise clusters. The tendency of the coal structure stabilization energies to be somewhat lower than the pairwise molecular interaction energies is believed to reflect the constraints of the covalent bonds between coal clusters, which tend to prevent fully-optimal ring overlap.

In earlier studies of hydrocarbon liquids, White found an excellent correlation between boiling point data and gas-chromatographic retention indices for 48 polyaromatic hydrocarbons (20). Such correlations are of value when evaluating the boiling fractions derived from coal liquefaction products. In this work, White did not consider partially- or fully-saturated ring compounds, which also would be important constituents in liquids from coal. Boiling points reflect generally the intermolecular forces, including vdW interactions, between molecules. In Fig. 2, the boiling points for the molecules represented in Fig. 1 (excluding perhydrocoronene, for which data were not found) are plotted against the vdW stabilization energies. The data separate into two quite distinct, relatively linear sets, one for aromatic and one for saturated ring compounds. Additional data would be necessary to determine whether such correlations are sufficiently accurate to provide predictive value for other ring compounds.

Discussion

Calculations of bituminous coal structures using CAMD techniques have demonstrated that intercluster vdW and hydrogen-bond interactions provide significant energy stabilization, with

vdW interactions apparently providing a larger total contribution to stabilization. The importance of vdW interactions for middle-rank coals has been pointed out previously (7,11), but not the possibility that vdW interactions actually may contribute more to energy stabilization than hydrogen bonds. The present calculations based on pairs of ring compounds show the relative effects of ring size and of ring saturation on vdW stabilization energy. These data support the increased strength of vdW interactions reported for higher-rank coals (11,12), for which the average ring size and the degree of aromaticity both increase. The ring pair data also have been shown to correlate reasonably well with boiling point data for a limited range of molecules, with aromatic ring compounds showing a distinctly different relationship than saturated ring compounds. It would be interesting to study partially-saturated rings and heteroatom-containing ring compounds as well, to provide additional data for comparison with coals and coal products.

The present studies were based on molecular models of coal, which do not incorporate the three-dimensional cross-linking that is believed to occur in actual coal structures. To address this issue, CAMD studies of coal as a network structure are planned. In these studies, representative molecular clusters (modified relative to the molecular structures considered in this work, to account for more recent chemical and structural data, refs. 21-23) will be linked together with intermittent cross-links, forming a three-dimensional structure. The structures will be energy minimized, and vdW and hydrogen bond interactions evaluated. Also, the physical density represented by the structures will be calculated, and the presence of void volume (microporosity) determined. Results will be correlated with various experimental data and with theoretical network models for coal.

Acknowledgements

References

1. Given, P. H., Fuel 1960, 39, 147.
2. Wiser, W. H., Proc. of the Electric Power Research Institute Conf. on Coal Catalysis, 1973.
3. Solomon, P. R., in New Approaches in Coal Chemistry, Am. Chem. Soc. Symp. Series No. 169, 1981; p. 61.
4. Shinn, J. H., Fuel 1984, 63, 1187.
5. Larsen, J. W., Am. Chem. Soc. Div. Fuel Chem. Preprints 1985, 30(4), 444.
6. Larsen, J. W., Green, T. K., and Kovac, J., J. Org. Chem. 1985, 50, 4729.
7. Brenner, D., Fuel 1985, 64, 167.
8. Solomon, P. R., Best, P. E., Yu, Z. Z., and Deshpande, G. V., Am. Chem. Soc. Div. Fuel Chem. Preprints 1989, 34(3), 895.
9. Hall, P. J., Marsh, H. and Thomas, K. M., Fuel 1988, 67, 863.
10. Lucht, L. M., and Peppas, N. A., Fuel 1987, 66, 803.
12. Mallya, N. and Stock, L. M., Fuel 1986, 65, 736.
13. White, C. M., and Schmidt, C. E., Fuel 1987, 66, 1030.
14. Carlson, G. A., Am. Chem. Soc. Div. Fuel Chem. Preprints 1989, 34(3), 780.
15. Fruhbeis, H., Klein, R., and Wallmeir, H., Angew. Chem. Int. Ed. Engl. 1987, 26, 403.
16. BioDesign, Pasadena, CA, unpublished data.
17. Carlson, G. A., "Modeling of Coal Structure Using Computer-Aided Molecular Design", to be published in the Given Symposium Advances in Coal Science series (1991).
18. Larsen, J. W., Am. Chem. Soc. Div. Fuel Chem. Preprints 1988, 33(1), 400.
19. Miller, J. H., Mallard, W. G., and Smyth, K. C., J. Phys. Chem. 1984, 88, 4963.
20. White, C. M., J. Chem. Eng. Data 1986, 31, 198.
21. Solum, M. S., Pugmire, R. J., and Grant, D. M., Energy & Fuels 1989, 3, 187.
22. Carlson, R. E., Brigham Young University, unpublished data.
23. Winans, R. E., Argonne National Laboratory, unpublished data.

Table I

HYDROGEN BONDS AND VAN DER WAALS INTERACTIONS IN COAL STRUCTURES

| Parameter	Wiser	Solomon	Shinn
Total # Atoms	394	396	1040
Hydrogen Bonds			
# H-Bond Acceptors	26	20	68
# H-Bond Donors	16	12	30
# Intercluster H-Bonds Formed	5	9	29
Δ H-Bond Energy	-25	-71	-130
Energy/Intercluster H-Bond	-5.0	-7.9	-4.5
Van der Waals Interactions			
Total # vdW Interactions	20451	21706	74882
Δ vdW Energy	-84	-119	-341
Energy/vdW Interaction	-.004	-.005	-.005
Energy Comparison			
Ratio $\dfrac{\Delta \text{ H-Bond Energy}}{\Delta \text{ vdW Energy}}$	.30	.60	.38

ↄ
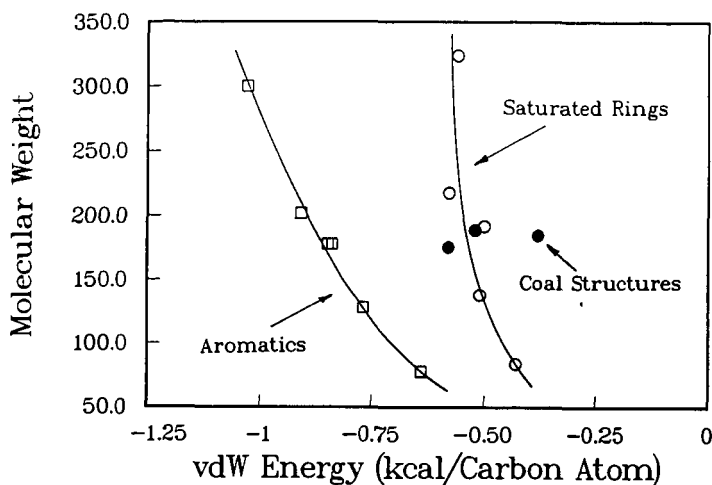
Fig. 1. Van der Waals stabilization energies for pairs of aromatics and saturated ring compounds as a function of molecular weight, and for bituminous coal structures as a function of cluster size. Lines are hand fits to data, drawn to aid the eye.
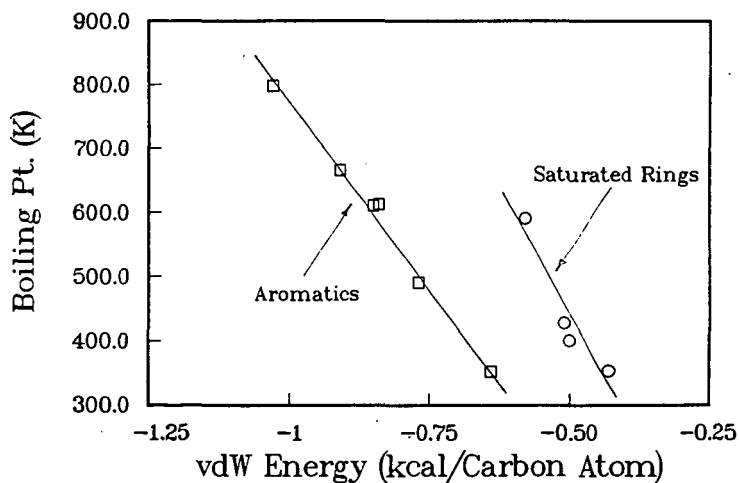

Fig. 2. Van der Waals stabilization energies for pairs of aromatics and saturated ring compounds, plotted as a function of boiling points. Straight lines are hand fits to data, drawn to aid the eye.